Kondo effect in transport through molecules adsorbed on metal surfaces: from Fano dips to Kondo peaks

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The Kondo effect observed in recent STM experiments on transport through CoPc and TBrPP-Co molecules adsorbed on Au(111) and Cu(111) surfaces, respectively, is discussed within the framework of a simple model (Phys. Rev. Lett. **97**, 076806 (2006)). It is shown that, in the Kondo regime and by varying the adequate model parameters, it is possible to produce a crossover from a conductance Kondo peak (CoPc) to a conductance Fano dip (TBrPP-Co). In the case of TBrPP-Co/Cu(111) we show that the model reproduces the changes in the shape of the Fano dip, the raising of the Kondo temperature and shifting to higher energies of the dip minimum when the number of nearest neighbors molecules is lowered. These features are in line with experimental observations indicating that our simple model contains the essential physics underlying the transport properties of such complex molecules.

Since the work of Madhavan *et al* [1] on the Kondo effect [2, 3] in transport through a Co atom adsorbed on an Au(111) surface, a great deal of attention has been devoted to investigate, both theoretical and experimentally, such effect in either isolated Co atoms [4, 5] or in Co-containing molecules [6, 7, 8, 9] adsorbed on metal surfaces. The possibility of tuning the Kondo temperature [6, 9] has been recently demonstrated, increasing considerably the interest of these systems. In particular it has been shown that, the characteristics, and even the existence, of the Kondo resonance can be controlled by distorting a CoPc molecule adsorbed on a Au(111) surface [6]. More recently [9] the Kondo temperature in a TBrPP-Co molecule adsorbed on a Cu(111) surface has been increased by decreasing the number of nearest-neighbor TBrPP-Co molecules. The authors of [9] argued that this is due to a reduction of surfaces states when the number of nearest neighbors molecules around a given one is increased.

One of the most interesting aspects of those two works is that while in the case of CoPc/Au(111) a Kondo peak was observed, in the experiments on TBrPP-Co/Cu(111) the conductance showed a Fano dip, as in isolated Co atoms adsorbed on metal surfaces [1, 4, 5]. Those two molecules, although largely different, have two outstanding similarities: i) both have the Co atom in the their geometric centers, and, ii) their STM images show four clearly defined lobes [6]. The enormous complexity of the electronic structure of these molecules and the many-body physics involved hinder a detailed account of these systems. One of the main goals of the present work is to show, using a simple model that catches the most prominent features of both molecules, under which circumstances dips or peaks appear in the transmission.

A model Hamiltonian was taken assuming the following small atomic arrangement [8]: a central site with a single atomic orbital, a strong Coulomb repulsion at the Co atom and four lobes of the molecule described by four atomic orbitals placed on a square, which center is the Co atom (see Fig. 1 of Ref. [8]). Two additional orbitals located above and below the Co atom are included to represent the apex of the STM tip and an atom on the metal surface, respectively.

The Hamiltonian investigated here takes the form,

$$\hat{H} = \sum_{i\sigma} \epsilon_i c_{i\sigma}^\dagger c_{i\sigma} + \sum_{<ij>;\sigma} t_{i,j} c_{i\sigma}^\dagger c_{j\sigma} + U n_{Co\uparrow} n_{Co\downarrow} \quad (1)$$

where $c_{i\sigma}^\dagger$ creates an electron at site i and spin σ and $n_{Co\sigma}$ is the occupation operator associated to Co. The cluster is connected to the STM tip and the metal surface both represented by energy independent self-energies. The parameter $t_{i,j}$ is the hopping between atomic orbitals located on sites i and j (the symbol $<>$ in Eq. (1) indicates that $i \neq j$), each orbital has an energy ϵ_i, and the local Coulomb repulsion on Co is described by U.

The hopping matrix elements incorporated in Ref. [8] were: $t_{Co,t}$ (Co/STM tip), $t_{Co,m}$ (Co/metal surface), $t_{Co,l}$ (Co/molecule lobes) $t_{l,l}$ (inter-lobe hopping) and $t_{l,m}$ (lobes/metal surface). In this work we incorporate an additional parameter: the direct hopping between the tip and the lobes $t_{t,l}$. The reason to do so is that Fano antiresonances appear whenever the main current flows through sites that have laterally attached strongly correlated sites [4, 10]. On the other hand, this is justified

by the fact that, in TBrPP-Co/Cu(111), the d_{z^2} orbital (the one that is likely responsible for the Kondo effect, see below) is much deeper than in CoPc/Au(111) (-0.7 and -0.15 eV, respectively) indicating that, in TBrPP-Co, $t_{t,l}$ and $t_{Co,t}$ may at least be comparable. One lead is attached to Co and describes the STM tip. The other lead (the metal surface) is attached to the surface atom below Co and to the lobes.

When the cluster is connected to electrodes, the transmission across the system is given by $T(E) = \frac{2e^2}{h} \text{Tr}[t^\dagger t]$ [11], and the conductance is $\mathcal{G} = T(E_F)$, where E_F is the Fermi level. In this expression, matrix t is $t = \Gamma_U^{1/2} G^{(+)} \Gamma_L^{1/2} = \left[\Gamma_L^{1/2} G^{(-)} \Gamma_U^{1/2}\right]^\dagger$, where $\Gamma_{U(L)} = i(\Sigma_{U(L)}^{(-)} - \Sigma_{U(L)}^{(+)})$, $\Sigma_{U(L)}^{(\pm)}$ being the self-energies of the upper (U) and lower (L) leads, STM tip and gold surface, respectively. Superscripts (+) and (-) stand for retarded and advanced. The Green function is written as [12], $G^{(\pm)} = \left(\left[G_0^{(\pm)}\right]^{-1} - \left[\Sigma_U^{(\pm)} + \Sigma_L^{(\pm)}\right]\right)^{-1}$, where $G_0^{(\pm)}$ is the Green function of the isolated cluster. In this work $G_0^{(\pm)}$ is obtained either by means of a finite U slave bosons (SB) approach [13, 14, 15, 16] or by exact diagonalization in which case the result corresponds to the Embedding Cluster Approximation (ECA) method [8, 10, 17, 18].

In carrying out calculations, we have taken the self-energies attached to the tip and metal site below Co $\Sigma_U^{(\pm)} = \mp 0.2i$ eV, whereas that attached to the lobes $\Sigma_L^{(\pm)} = \mp t_{l,m}^2 \rho_m i$, where ρ_m is the density of states at the metal surface that will be varied to simulate the presence or absence of surface states. In addition we assume half-filling (one electron per site) and take $\epsilon_{Co} = -U/2$ and the rest of atomic orbitals lying at zero energy (hereafter the Fermi level E_F of the whole system will be taken as the zero of energies).

Other model parameters have been varied aiming to identify their role in the behavior of this system, but always over ranges such that the main features in the conductance occur in energy scales similar to the experimental ones [9]. It is worth mentioning that in the present work U was taken always smaller than 3 eV, while in [8] a value of 8 eV was assumed. We note that the latter value is probably too large, as indicated by a recent study of atomic Co on a Cu(100) surface [5]. Although screening in the Co/Cu(100) is probably more important than in the present case, we adopt the more conservative lower values. All calculations were done at zero temperature.

The results depicted in Fig. 1 illustrate how switching on the lobe/tip hopping produces a crossover from a Kondo peak to a Fano dip. In order to make more apparent the crossover we took $t_{Co,m}=0$. The crossover is also clearly noted in the numerical results for the non-diagonal elements of the density matrix shown in Fig. 1c. The latter is calculated using the standard expres-
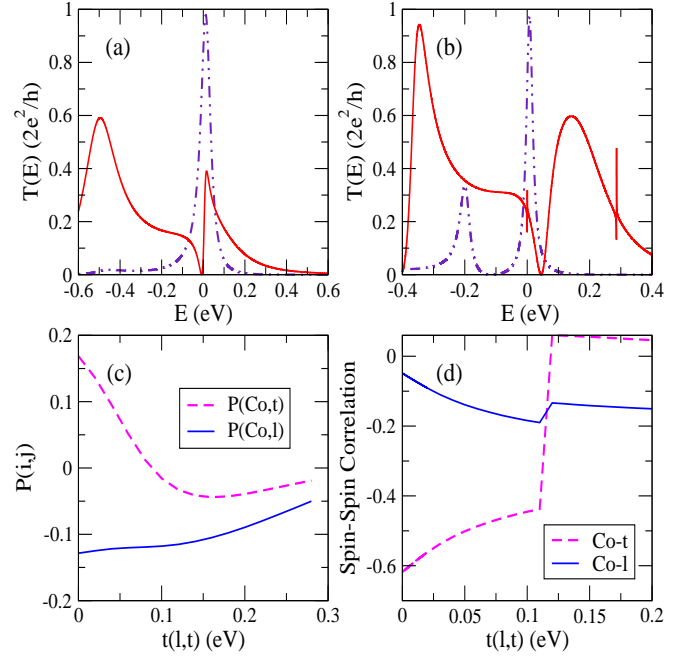

FIG. 1: (Color on line). Upper panels: transmission $T(E)$ (in units of the conductance quantum) versus the energy E (in eV) referred to the Fermi energy, calculated by means of the SB (a) and the ECA (b) methods (see text); results for $t_{l,t} = 0$ (green chain line) $t_{l,t} = 0.08$ eV (continuous red line) are shown. (c) Non-diagonal elements of the density matrix versus $t_{l,t}$ as calculated by means of the SB approach. (d) Spin-spin correlation versus $t_{l,t}$ calculated by means of the ECA method. The rest of the parameters used in the calculations are: $t_{Co,t} = 0.08eV$, $t_{Co,l} = -0.14eV$, $t_{Co,m} = 0$, $t_{l,l} = -0.2eV$, $t_{l,m} = 0.14eV$, $U = 1.6$ eV and $\rho_m = 5eV^{-1}$.

sion, $P(i,j) = \frac{1}{2\pi} \int_{-\infty}^{\infty} G^<(i,j;E)dE$, where $G^<(i,j;E)$ is the lesser Green function of the whole system. It is noted that $P(Co,t)$ is strongly reduced and tends to zero as the lobes/tip hopping becomes $t_{l,t} > t_{Co,t}$, triggering the crossover in the transmission from a Kondo peak to a Fano dip. This indicates that, in the latter situation, the current flowing through the Co reduces significantly. There is a concomitant small reduction of $P(Co,l)$ that however, remains significantly greater (in absolute value) than $P(Co,t)$ for $t_{l,t} > t_{Co,t}$, as shown in the figure. The drastic reduction of the tip/Co current permits the appearance of a destructive interference among the electrons going directly from the tip to the metal through the lobes and those performing the same trajectory but visiting the Co atom. This last path is possible due to the Kondo resonance located at the Co. From this point of view the Co atom acts as a correlation impurity laterally coupled to the conduction channel. On the other hand, the results for the spin-spin correlation calculated with the ECA method shown in Fig. 1d clearly indicate that the strong anti-ferromagnetic correlation between Co and the tip characteristic of the Kondo regime for $t_{Co,t} > t_{t,l}$ [8] is destroyed as $t_{t,l}$ increases. In this
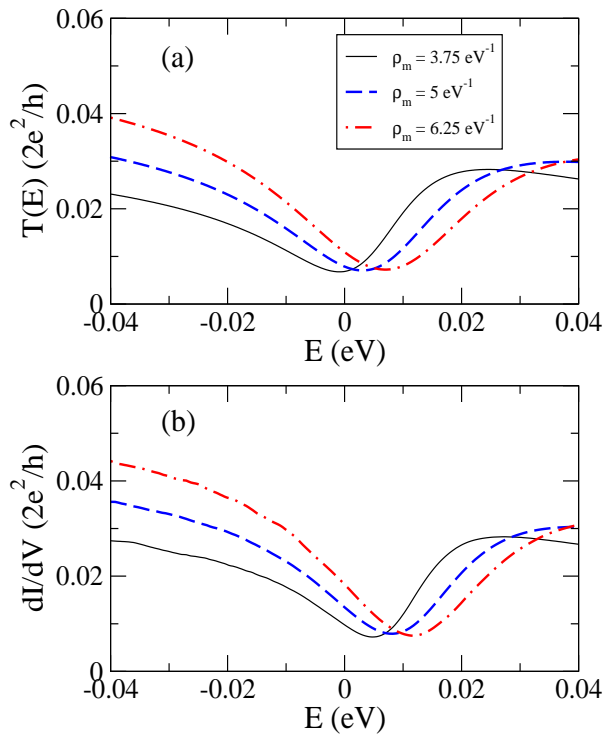
FIG. 2: (Color on line). Transmission $T(E)$ (a) and differential conductance dI/dV (b) (both in units of the conductance quantum) versus either the energy E referred to the Fermi energy or the bias potential V_{bias} (in eV) as calculated by means of the SB method. Results for three values of the metal density of states are shown. The rest of the model parameters used in the calculations are: $t_{Co,m} = 0.04$ eV, $t_{Co,l} = -0.14$ eV, $t_{Co,t} = 0.04$ eV, $t_{l,l} = -0.2$ eV, $t_{l,m} = 0.14$ eV, $t_{l,t} = 0.032$ eV and $U = 1.6$ eV.

case the Kondo regime is driven by the Co/lobes correlation that remains always anti-ferromagnetic. It is worth noting that the spin-spin correlation shown in the figure changes abruptly because it corresponds to the isolated cluster which is exactly diagonalized when the ECA method is used.

Results obtained by means of either the SB or ECA methods (Fig. 1a,1b) are very similar, they only differ at a quantitative level. The noticeable differences between the two approaches make this agreement particularly relevant. On the other hand, although both methods are reliable around the Fermi level, only the SB approach allows an easy implementation of Keldysh formalism [12] to treat the out-of-equilibrium problem, as discussed below. Taking note of the latter, and recalling that the SB method is numerically faster, the results presented and discussed hereafter are all obtained with that method. In the case of the Fano dip, we note the presence of a broad peak at around -0.5 eV. This peak almost coincides with that observed experimentally at -0.7 eV that was ascribed to the d_{z^2} orbital, the one probably responsible of the strong correlation effects discussed here (see also below).

It should be note that, the latter peak shows up below E_F if both $t_{l,l}$ and $t_{Co,l}$ are negative. When they are assumed to be positive the results change to $T(-E)$ and if only one of them is negative the transmission is modified resembling less the experimental observations (a wider dip and a narrower peak below E_F).

As remarked above, it was suggested in [9] that there is a correlation between the number of nearest neighbors nn around a molecule and the density of states ρ_m seen by the peripheral atoms of the molecule (the larger nn the smaller ρ_m). The effects of varying the density of states at the metal surface on the Fano dip are illustrated in Fig. 2. In these calculations we have taken a value of $t_{Co,m}$ similar to that of $t_{Co,t}$ as it seems more realistic. Results for the transmission versus energy are shown in the upper panel, whereas the differential conductance versus bias voltage is shown in the lower panel. They were calculated by implementing Keldysh formalism into the SB approach along the lines discussed in Ref. [19]. It is noted that the two results are remarkably similar, as expected whenever the bias voltage is not very large [20]. This supports the validity of the comparison of the transmission $T(E)$ with the experimental results associating the external applied field to the variable E. In figure 2 we note that, increasing the density of states, the Fano antiresonance becomes wider and dipper and shifts to higher voltages. The first effect implies an increase of the Kondo temperature, in agreement with the proposal made in Ref. [9]. Concerning the shift, it was mentioned in [9] that the voltage at which the minima in the Fano dips occurred, changed when the number of neighboring molecules was varied, although unfortunately a well-defined tendency was not mentioned. We also note changes in the shape of the dip (particularly in the relative height of the left and right shoulders) also observed in the experimental study of Ref. [9].

Fig. 3a further illustrates the crossover from Fano dip to Kondo peak investigated in this work. The figure depicts results for the transmission versus energy for three values of the lobes/tip hopping, namely, $t_{l,t}=$ -0.18 eV, 0.0 and 0.06 eV. The transmission pattern changes from Fano dip-like to Kondo peak-like and back to Fano dip-like. This behavior resembles the results reported in [4] which showed a similar oscillation of the tunneling DOS as the distance from the tip to the impurity (a Co atom adsorbed on a metal surface) was varied. Increasing the Coulomb repulsion parameter U (see Fig. 3c) sharpens both the Fano dip and the Kondo peak, although scarcely affects the structure away the Fermi level that shows up in the first case. The sharpening of the structures results from the reduction of the Kondo temperature when U is increased. It is interesting to note that the Fano antiresonance coexists with the broad peak below the Fermi level, while the Kondo peak does not. This is further illustrated by the transmission results shown in Fig. 3b for two values of the lobe/lobe hopping. The results are
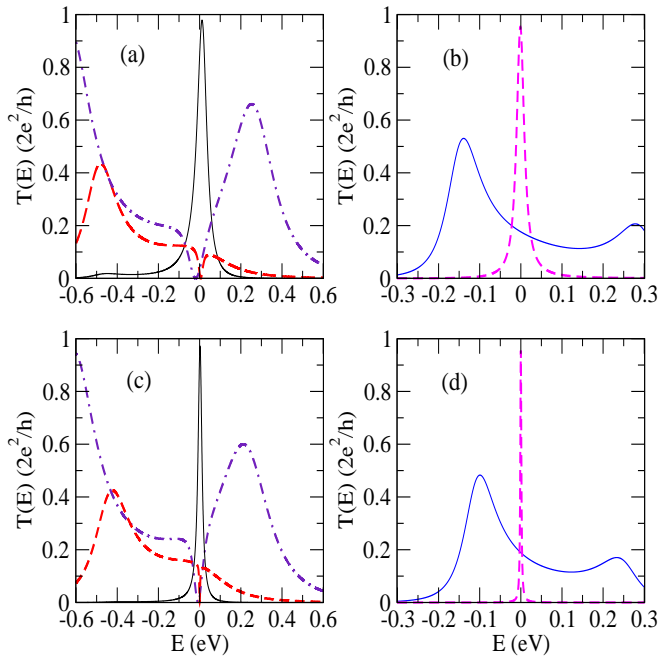
FIG. 3: (Color on line). Transmission $T(E)$ (in units of the conductance quantum) versus the energy E (in eV) referred to the Fermi energy, calculated by means of the SB method (see text). The parameters used in the calculations are hereafter given: $t_{Co,m} = 0.0$ eV, $t_{Co,l} = -0.14$ eV, $t_{Co,t} = 0.08$ eV. Left panels: $t_{l,l} = -0.2$ eV, $t_{l,m} = 0.14$ eV, $t_{l,t}$=-0.18 eV (green chain line) 0 eV (continuous black line) and 0.06 eV (broken red line) and $U = 1.6$ eV (a) and $U = 2.3$ eV (c). Right panels: $t_{l,l} = 0.05$ eV (continuous blue line) and 0.3 eV (broken magenta line), $t_{l,m} = 0.14$ eV, $t_{l,t} = 0.0$ eV, and $U = 1.6$ eV (b) and $U = 2.3$ eV (d).

conclusive: the well defined Kondo peak that shows up for the larger value of $t_{l,l}$, transforms into a much broader feature peaked at around -0.15 eV when that hopping is reduced. Note that the latter feature may actually be that reported in [6] for the undistorted molecule which, as pointed out before, does not show a Kondo peak. The effects of increasing U (see Fig. 3d) are similar to those noted in the case of Fig 3c.

Summarizing, with the help of a simple model we have been able to discuss the main features of the Kondo regime observed either as a Fano dip in TBrPP-Co/Cu(111) or as a Kondo peak in CoPc/Au(111). We showed that, by varying some of the model parameters, it was possible to produce a crossover in the conductance from a Fano dip to a Kondo peak. The model not only allows to discuss the physics around the Fermi level, but in the Kondo regime also accounts for features in the experimental conductance that coexist with the Fano dip, or does not exist when the transmission has a peak. In addition, we have been able to confirm the role of the sur-

face density of states in defining the Kondo temperature in the TBrPP-Co/Cu(111), as suggested by the authors of that study. Our analysis illustrates the usefulness of simple models in which strong correlation effects preclude a full *ab initio* study.

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